

## PATENT ABSTRACTS OF JAPAN

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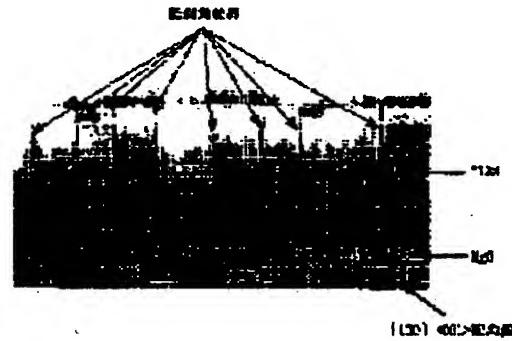
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## (54) SUPERCONDUCTING WIRE HAVING HIGH CRITICAL CURRENT DENSITY

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To improve critical current density in a magnetic field by the introduction of low inclination grain boundaries into a superconducting oxide film by forming a biaxially oriented superconducting oxide film on a metallic silver substrate having a {100} <001> texture.

**SOLUTION:** An oxide intermediate layer biaxially oriented in a substrate plane, a parallel plane of a substrate is proper in {100}, and magnesium oxide MgO is used as a material. When a lattice miss fit of oxide and superconducting oxide of this intermediate layer is high like 6 to 11%. The superconducting oxide growing on the oxide of the intermediate layer performs pseudo epitaxial growth having fluctuation in in-plane orientation. Due to this fluctuation, low inclination grain boundaries less than one degree of an inclination of a degree of not interrupting a path of a superconducting current, are generated in large numbers in a C axis oriented superconducting oxide film manufactured on the oxide of the intermediate layer. Since these low inclination grain boundaries operate as pin fastening points to trap a magnetic field, high critical current density in the magnetic field can be realized.



## LEGAL STATUS

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## CLAIMS

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[Claim(s)]

[Claim 1] A superconduction wire rod with the superconduction oxide film formed on the metal silver substrate with the {100 <001>} texture in which the oxide interlayer who did biaxial orientation in the substrate side was formed.

[Claim 2] Said superconduction oxide film is a superconduction wire rod according to claim 1 characterized by having Y123 mold crystal structure.

[Claim 3] The presentation of said oxide film () [ RE1aRE2b ] .... REnBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+d</sub>, RE1!=RE2! = ..... !=REn (RE1, RE2, and .... REn =Y, and La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb) (), [ a+b+] .... +l=1 and 0 <= -- a, b, and .... the superconduction wire rod according to claim 1 or 2 characterized by being l=1.

[Claim 4] The superconduction wire rod according to claim 1 or 2 with which the presentation of said oxide film is characterized by being RE<sub>1+x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>6+d</sub> (RE = La, Pr, Nd, Sm, Eu, Gd) (-0.05<=x<=0.2).

[Claim 5] The superconduction wire rod according to claim 1 characterized by the grid misfit of said oxide interlayer and said superconduction oxide being 6 – 11%.

[Claim 6] Said oxide interlayer is a superconduction wire rod according to claim 1 characterized by a field parallel to a substrate being {100}.

[Claim 7] Said oxide interlayer is a superconduction wire rod according to claim 1 characterized by being a magnesium oxide.

[Claim 8] Said oxide interlayer is a superconduction wire rod according to claim 1 characterized by being the magnesium oxide whose field parallel to a substrate is {100}.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the superconduction wire rod which has high critical current density.

**[0002]**

**[Description of the Prior Art]** the former -- oxide superconductivity -- about the conductor, in order to raise a superconduction property, especially the critical-current-density  $J_c$  property in the inside of a magnetic field, various examination is made, and the various manufacture approaches are proposed until now.

**[0003]** In order to obtain high critical current density with a superconduction wire rod, it is necessary to carry out biaxial orientation of the superconduction oxide film. Therefore, a solid phase technique, a gaseous-phase method, and the approach of carrying out epitaxial growth of the superconduction oxide film according to various processes of a liquid phase process are common on a single crystal, the oxide substrate which carried out orientation within a field, and a metal substrate.

**[0004]**

**[Problem(s) to be Solved by the Invention]** Although the formation of a long wire rod is possible for the metal silver which has the {100 <001>} texture produced by the rolling-out method in manufacture of a superconduction wire rod If epitaxial growth of the superconduction oxide film is besides carried out directly, J.D.Budai and others As Appl.Phys.Lett.57 1836 (1993) have reported, orientation within a field is not carried out. Since a high inclination grain boundary was formed, it was difficult to obtain high critical current density all over a magnetic field.

**[0005]** The technical problem which this invention tends to solve is making it possible to obtain the superconduction oxide film which has high critical current density on the metal silver substrate in which high critical-current-density-ization has the difficult {100 <001>} texture all over a magnetic field with the conventional technique.

**[0006]**

**[Means for Solving the Problem]** In order that this invention may solve the above-mentioned technical problem, it forms the interlayer of the oxide which carried out orientation within a field between the superconduction oxide film and a substrate, and grows up the superconduction oxide film on it. Consequently, the superconduction wire rod which has the superconduction oxide film on a metal silver substrate with the {100 <001>} texture in which the oxide interlayer who did biaxial orientation in the substrate side was formed is obtained.

**[0007]** Since biaxial orientation of the superconduction oxide film produced on the oxide interlayer who made it grow up so that a field parallel to a substrate on metal silver with {100 <001>} texture may become {100} bearings is carried out, it becomes producible [ the superconduction wire rod which has the superconduction oxide film of the long picture which has high critical current density ]. Especially the formation approach of the oxide film which carried out orientation within a field, and the superconduction oxide film is not limited.

**[0008]** As superconduction oxide film, there is oxide film which has Y123 mold crystal structure. and this oxide film -- a presentation -- Ba(RE<sub>1</sub>aRE<sub>2</sub>b ..... RE<sub>n</sub>)<sub>2</sub>Cu<sub>3</sub>O<sub>6+d</sub> and RE<sub>1</sub>=RE<sub>2</sub>= ..... !

=REn (RE1, RE2, and .... REn = Y, and La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb) --- (--- a+b+ .... +l=1 and 0 <= --- a, b, and .... it is l <=1).

[0009] Moreover, RE<sub>1+x</sub>Ba<sub>2-x</sub>Cu<sub>3</sub>O<sub>6+d</sub> (RE = La, Pr, Nd, Sm, Eu, Gd) and the thing of (-0.05 <= x <= 0.2) are also used for a presentation as other superconduction oxide film.

[0010] A field parallel to a substrate is suitable for {100}, and a magnesium oxide is suitable for the oxide interlayer who did biaxial orientation in the substrate side as an ingredient. The magnesium oxide whose field parallel to a substrate is {100} does better effectiveness so.

[0011] The oxide interlayer who did biaxial orientation in the substrate side does so effectiveness with the sufficient time of grid misfit with a superconduction oxide being 6 - 11%. When the grid misfit of an interlayer's oxide and a superconduction oxide is as high as 6 - 11%, the superconduction oxide film which grows on an interlayer's oxide carries out pseudo-epitaxial growth which has fluctuation in the orientation within a field.

[0012] The inclination of extent which does not interrupt the pass of supercurrent as shown in the superconduction oxide film which is produced on an interlayer's oxide for this fluctuation, and which carried out c axis orientation at drawing 1 arises [ many less than 1-degree low inclination grain boundaries ]. Since it worked as a pinning point that this low inclination grain boundary carries out the trap of the magnetic field, high critical-current-density-ization all over a magnetic field was attained.

[0013] It is important for a metal silver substrate here to have {100 <001>} texture. Construction material does not necessarily need to be a pure metal and the metal complex which carried out detailed distribution of an alloy or the ceramics is contained.

[0014]

#### [Embodiment of the Invention]

Example 1 substrate prepared the metal silver tape with {100 <001>} texture, and the MgO interlayer formed by RF spatter. The grid misfit between Ag (100) and MgO (100) is about 3%. Substrate temperature set 700 degrees C, the pressure of 1.6Pa, and the output to 200W. A MgO interlayer's thickness was set to 3000. Having carried out orientation within a field of the MgO was checked. PLD which besides used Y123 target --- 1 micrometer was formed for Y123 film by law. moreover --- without it forms a MgO interlayer for a comparison --- a metal silver tape top --- direct Y123 --- PLD --- the sample which formed membranes by law was also prepared. It was not concerned with a MgO interlayer's existence, but what carried out c axis orientation of Y123 was obtained.

[0015] The pole figure of the field (103) of Y123 film is shown in drawing 2. Although what formed Y123 directly on the metal silver tape showed the symmetry 8 times, what formed membranes on the MgO interlayer showed the symmetry 4 times, and it was checked that the orientation within a field had been taken. The result of having measured the critical current density in the inside of a magnetic field after oxygen annealing to drawing 3 is shown. Critical current density of the sample [ in which the MgO interlayer was formed ] improved substantially.

[0016]

[Effect of the Invention] Growth of the superconduction oxide film which carried out biaxial orientation on metal silver with {100 <001>} texture by the process of the superconduction wire rod of this invention was able to be enabled, and the critical current density of the superconduction oxide film in the inside of the magnetic field by the low inclination grain boundary installation to the superconduction oxide film was able to be raised further.

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**TECHNICAL FIELD**

---

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**PRIOR ART**

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**EFFECT OF THE INVENTION**

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**TECHNICAL PROBLEM**

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**MEANS**

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## DESCRIPTION OF DRAWINGS

### [Brief Description of the Drawings]

[Drawing 1] It is drawing showing the cross-section structure of the superconduction wire rod of this invention.

[Drawing 2] It is the pole figure of the field (103) of Y123 film of the superconduction wire rod of this invention.

[Drawing 3] It is the graph of the critical current density in the inside of the magnetic field of the superconduction wire rod after oxygen annealing.

[Translation done.]

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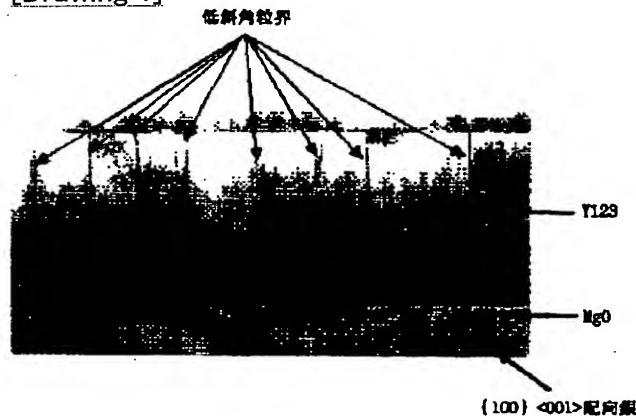
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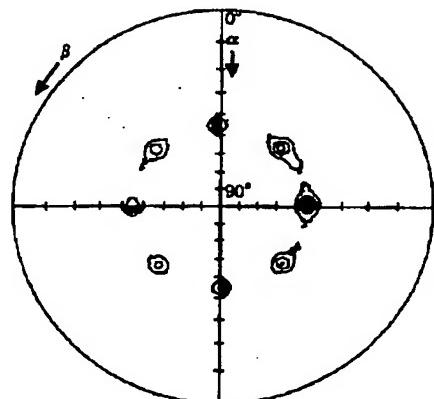
## DRAWINGS

### [Drawing 1]

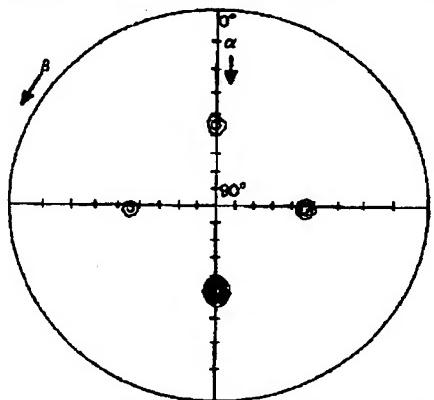


(1) (100) <001>配向軸/MgO/Y123

### [Drawing 2]

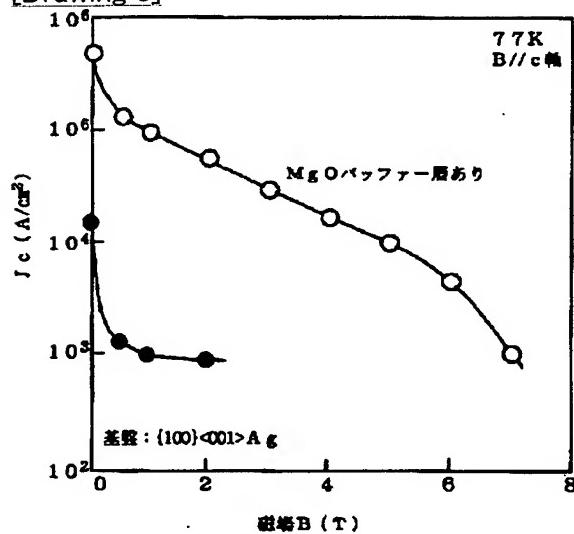


(1) MgOバッファーレー層がない場合のY123(103)極点



(2) MgOバッファーレー層がある場合のY123(103)極点

## [Drawing 3]



[Translation done.]

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愛知県名古屋市東区東新町1番地

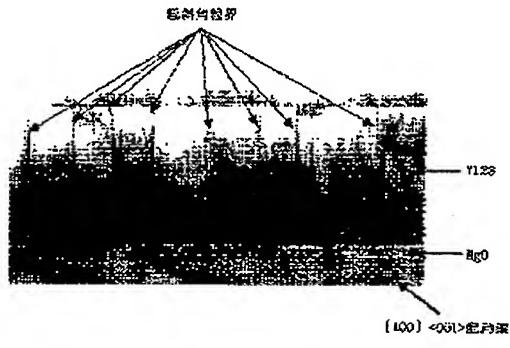
(74) 代理人 弁理士 豊田 正雄

最終頁に続く

(54) 【発明の名称】 高臨界電流密度をもつ超電導線材

## (57) 【要約】

【課題】 磁場中で高臨界電流密度化が困難であった{100}<001>集合組織を持つ金層銀基板上で高い臨界電流密度を有する超電導酸化物膜を有する超電導線材を得る。  
 【解決手段】 基板面内で2軸配向した酸化物中間層が形成された{100}<001>集合組織を持つ金層銀基板上に形成されたY123型結晶構造を有する超電導酸化物膜を持つ超電導線材とする。



{100} &lt;001&gt;配向層

(2)

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2

## 【特許請求の範囲】

【請求項1】基板面内で2軸配向した酸化物中間層が形成された $\{100\}<001>$ 集合組織を持つ金層銀基板上に形成された超電導酸化物膜を持つ超電導線材。

【請求項2】前記超電導酸化物膜は、Y123型結晶構造を有することを特徴とする請求項1記載の超電導線材。

## 【請求項3】前記酸化物膜の組成が

$(RE_1aRE_2b,\dots,RE_n)Ba_2Cu_3O_{6+d}$ ,  $RE_1 \neq RE_2 \neq \dots \neq RE_n$  ( $RE_1, RE_2, \dots, RE_n = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb$ ),  $(a+b+\dots+n=1, 0 \leq a, b, \dots, n \leq 1)$

であることを特徴とする請求項1または2記載の超電導線材。

## 【請求項4】前記酸化物膜の組成が

$RE_1+xBa_2-xCu_3O_{6+d}$  ( $RE = La, Pr, Nd, Sm, Eu, Gd$ ),  $(-0.05 \leq x \leq 0.2)$

であることを特徴とする請求項1または2記載の超電導線材。

【請求項5】前記酸化物中間層と前記超電導酸化物との格子ミスマッチが6~11%であることを特徴とする請求項1記載の超電導線材。

【請求項6】前記酸化物中間層は、基板に平行な面が $\{100\}$ であることを特徴とする請求項1記載の超電導線材。

【請求項7】前記酸化物中間層は、酸化マグネシウムであることを特徴とする請求項1記載の超電導線材。

【請求項8】前記酸化物中間層は、基板に平行な面が $\{100\}$ である酸化マグネシウムであることを特徴とする請求項1記載の超電導線材。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、高臨界磁流密度を有する超電導線材に関する。

## 【0002】

【従来の技術】従来より、酸化物超電導体については、超電導特性、特に磁場中の臨界磁流密度Jc特性向上させるために様々な検討がなされてきており、これまでに種々の製造方法が提案されている。

【0003】超電導線材で高い臨界電流密度を得るためにには超電導酸化物膜を2軸配向させる必要がある。そのため、単結晶や面内配向した酸化物基板、金属基板上に固相法、気相法、液相法のさまざまなプロセスにより超電導酸化物膜をエピタキシャル成長させる方法が一般的である。

## 【0004】

【発明が解決しようとする課題】超電導線材の製造において、圧延法で作製される $\{100\}<001>$ 集合組織を持つ金属銀は長尺線材化が可能であるが、この上に超電導酸化物膜を直接エピタキシャル成長させると、J. D. BudaiらがAppl. Phys. Lett. 57 1835 (1993)で報告しているように面内配向せず、高傾角粒界が形成されるため、

磁場中で高い臨界磁流密度を得るのが困難であった。

【0005】本発明が解決しようとする課題は、従来技術では磁場中で高臨界磁流密度化が困難であった $\{100\}<001>$ 集合組織を持つ金属銀基板上で高い臨界磁流密度を有する超電導酸化物膜を得ることを可能とすることである。

## 【0006】

【課題を解決するための手段】本発明は、上記課題を解決するため、超電導酸化物膜と基板の間に面内配向した酸化物の中間層を形成し、その上に超電導酸化物膜を成長させる。この結果、基板面内で2軸配向した酸化物中間層が形成された $\{100\}<001>$ 集合組織を持つ金属銀基板上に超電導酸化物膜を持つ超電導線材が得られる。

【0007】 $\{100\}<001>$ 集合組織を持つ金属銀上に基板に平行な面が $\{100\}$ 方位になるように成長させた酸化物中間層上に作製した超電導酸化物膜は2軸配向するので、高臨界磁流密度を有する長尺の、超電導酸化物膜を有する超電導線材の作製が可能となる。面内配向した酸化物膜および超電導酸化物膜の形成方法は、特に限定しない。

【0008】超電導酸化物膜としては、Y123型結晶構造を有する酸化物膜がある。そして、この酸化物膜は、組成が

$(RE_1aRE_2b,\dots,RE_n)Ba_2Cu_3O_{6+d}$ ,  
 $RE_1 \neq RE_2 \neq \dots \neq RE_n$   
 $(RE_1, RE_2, \dots, RE_n = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb)$ ,  
 $(a+b+\dots+n=1, 0 \leq a, b, \dots, n \leq 1)$

である。  
36 【0009】また、他の超電導酸化物膜として、組成が  
 $RE_1+xBa_2-xCu_3O_{6+d}$   
 $(RE = La, Pr, Nd, Sm, Eu, Gd)$ ,  
 $(-0.05 \leq x \leq 0.2)$

のものも用いられる。

【0010】基板面内で2軸配向した酸化物中間層は、基板に平行な面が $\{100\}$ が適当であり、材料としては酸化マグネシウムが適当である。基板に平行な面が $\{100\}$ である酸化マグネシウムはよりよい効果を奏する。

【0011】基板面内で2軸配向した酸化物中間層は、  
40 酸化物との格子ミスマッチが6~11%であるときよい効果を奏する。中間層の酸化物と超電導酸化物との格子ミスマッチが6~11%高い場合、中間層の酸化物上に成長する超電導酸化物膜は面内配向にゆらぎを持つ非エピタキシャル成長をする。

【0012】このゆらぎのために中間層の酸化物上に作製する2軸配向した超電導酸化物膜には図1に示すような超電導電流のバスを巡らない程度の傾角が1°未満の低傾角粒界が多数生じる。この低傾角粒界が磁場をトラップするピン止め点として働くため、磁場中の高臨界磁流密度化が可能となった。

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\* したが、Mgの中間層上に成膜したものは、4回対称を示し、面内配向がとれたことが確認された。図3に酸素アニール後に磁場中の臨界電流密度を測定した結果を示す。Mgの中間層を形成したサンプルは、臨界電流密度が大幅に向上了。

【0016】

【発明の効果】本発明の超電導線材の製法により、 $\{100\} <001>$ 集合組織を持つ金属銀上に2軸配向した超電導酸化物膜の成長を可能とし、さらに超電導酸化物膜への低傾角粒界導入による磁場中の超電導酸化物膜の臨界電流密度向上させることができた。

【図面の簡単な説明】

【図1】本発明の超電導線材の断面構造を示す図である。

【図2】本発明の超電導線材のY123膜の(103)面の極点図である。

【図3】酸素アニール後の超電導線材の磁場中の臨界電流密度のグラフである。

【0013】ここでいう金属銀基板は、 $\{100\} <001>$ 集合組織を持つものであることが重要である。材質は必ずしも純金属である必要はなく、合金やセラミックスを微細分散させた金属複合体なども含まれる。

【0014】

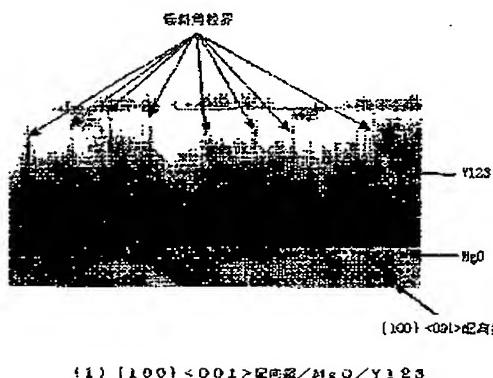
【発明の実施の形態】

実施例1

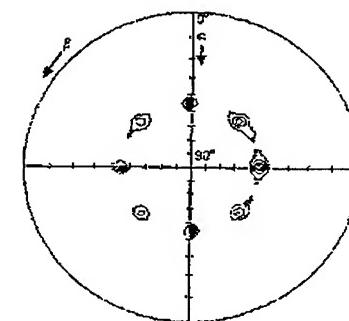
基板は $\{100\} <001>$ 集合組織を持つ金属銀テープを用意し、Mgの中間層はRFスパッタ法により形成した。Ag(100)とMg(100)の間の格子ミスマッチは約3%である。基板温度は700°C、圧力1.6Pa、出力は200Wとした。Mgの中間層の厚みは30nmとした。Mgは面内配向したことが確認された。この上にY123ターゲットを用いたPLD法によりY123膜を1μmを形成した。また比較のためMgの中間層を形成しないで、金属銀テープ上に直接Y123をPLD法で成膜したサンプルも用意した。Mgの中間層の有無に関わらず、Y123は面内配向したものが得られた。

【0015】図2にY123膜の(103)面の極点図を示す。金属銀テープ上に直接Y123を成膜したものは8回対称を示す。

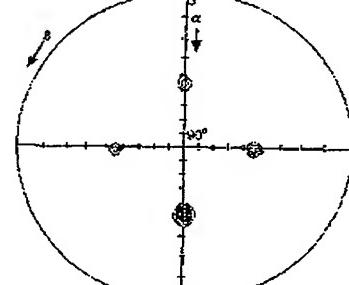
【図1】

(1)  $\{100\} <001>$  集合組織/MgO/Y123

【図2】



(1) MgOバッファー層がない場合のY123(103)極点

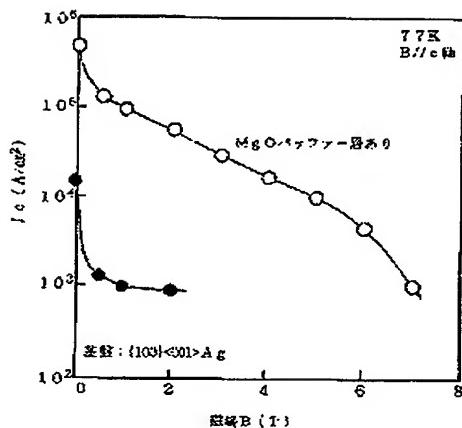


(2) MgOバッファー層がある場合のY123(103)極点

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[図3]



## フロントページの続き

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